CDT 1744

PROCESS FOR THE HYDRODESULFURIZATION
OF NAPHTHA

BACKGROUND OF THE INVENTION

Field of the Invention

5   This application claims priority from the prior U.S. provisional application, serial no. 60/454,259 filed 03/13/2003.

The present invention relates to the hydrodesulfurization of a full boiling range naphtha which contains organic nitrogen compounds. More particularly the invention relates to an improvement in the process for treating a fluid cracked naphtha to 10   remove organic sulfur compounds by hydrodesulfurization. Most particularly the invention relates to catalytic distillation column reactions and the restriction of organic nitrogen compounds from contact with the hydrotreating catalyst.

Related Information

Petroleum distillate streams contain a variety of organic chemical 15   components. Generally the streams are defined by their boiling ranges which determine the compositions. The processing of the streams also affects the composition. For instance, products from either catalytic cracking or thermal cracking processes contain high concentrations of olefinic materials as well as saturated (alkanes) materials and polyunsaturated materials (diolefins). Additionally, 20   these components may be any of the various isomers of the compounds.

The composition of untreated naphtha as it comes from the crude still, or straight run naphtha, is primarily influenced by the crude source. Naphthas from paraffinic crude sources have more saturated straight chain or cyclic compounds. As a general rule most of the "sweet" (low sulfur) crudes and naphthas are paraffinic. 25   The naphthenic crudes contain more unsaturates and cyclic and polycylic compounds. The higher sulfur content crudes tend to be naphthenic. Treatment of the different straight run naphthas may be slightly different depending upon their composition due to crude source.
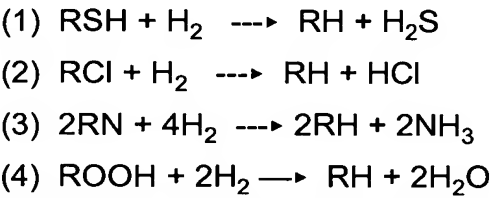
Reformed naphtha or reformate generally requires no further treatment except 30   perhaps distillation or solvent extraction for valuable aromatic product removal.

1

Reformed naphthas have essentially no sulfur contaminants due to the severity of their pretreatment for the process and the process itself.

Cracked naphtha as it comes from the catalytic cracker has a relatively high octane number as a result of the olefinic and aromatic compounds contained therein. In some cases this fraction may contribute as much as half of the gasoline in the refinery pool together with a significant portion of the octane.

Catalytically cracked naphtha gasoline boiling range material currently forms a significant part ($\approx$ 1/3) of the gasoline product pool in the United States and it provides the largest portion of the sulfur. The sulfur impurities may require removal, usually by hydrotreating, in order to comply with product specifications or to ensure compliance with environmental regulations.

The most common method of removal of the sulfur compounds is by hydrodesulfurization (HDS) in which the petroleum distillate is passed over a solid particulate catalyst comprising a hydrogenation metal supported on an alumina base. Additionally copious quantities of hydrogen are included in the feed. The following equations illustrate the reactions in a typical HDS unit:

(1) $RSH + H_2 \longrightarrow RH + H_2S$

(2) $RCl + H_2 \longrightarrow RH + HCl$

(3) $2RN + 4H_2 \longrightarrow 2RH + 2NH_3$

(4) $ROOH + 2H_2 \longrightarrow RH + 2H_2O$

Typical operating conditions for the HDS reactions are:

Temperature, °F	600-780
Pressure, psig	600-3000
H_2 recycle rate, SCF/bbl	1500-3000
Fresh H_2 makeup, SCF/bbl	700-1000

The reaction of organic sulfur compounds in a refinery stream with hydrogen over a catalyst to form H_2S is typically called hydrodesulfurization. Hydrotreating is a broader term which includes saturation of olefins and aromatics and the reaction of organic nitrogen compounds to form ammonia. However hydrodesulfurization is included and is sometimes simply referred to as hydrotreating.

After the hydrotreating is complete, the product may be fractionated or simply flashed to release the hydrogen sulfide and collect the now desulfurized naphtha.

The predominant light or lower boiling sulfur compounds are mercaptans while the heavier or higher boiling compounds are thiophenes and other heterocyclic compounds. The separation by fractionation alone will not remove the mercaptans. However, in the past the mercaptans were frequently removed by oxidative processes involving caustic washing. A combination oxidative removal of the mercaptans followed by fractionation and hydrotreating of the heavier fraction is disclosed in U.S. patent 5,320,742. In the oxidative removal of the mercaptans the mercaptans are converted to the corresponding disulfides.

In addition to treating the lighter portion of the naphtha to remove the mercaptans the lighter fraction traditionally has been used as feed to a catalytic reforming unit to increase the octane number if necessary. Also the lighter fraction may be subjected to further separation to remove the valuable C_5 olefins (amylenes) which are useful in preparing ethers.

More recently a new technology has allowed for the simultaneous treatment and fractionation of petroleum products, including naphtha, especially fluid catalytically cracked naphtha (FCC naphtha). See, for example, commonly owned U.S. patents 5,510,568; 5,597,476; 5,779,883; 5,807,477 and 6,083,378.

It has long been known that the organic nitrogen compounds inhibit the hydrodesulfurization reaction and to some extent the hydrogenation reaction. See for example "Poisoning of Thiophene Hydrodesulfurization by Nitrogen Compounds" by Vito LaVopa and Charles N. Satterfield published in the *Journal of Catalysis*, volume 110 (1988) at pages 375-387. In addition the effect of water and ammonia on hydrotreating catalysts has been studied. See "Influence of Water and Ammonia on Hydrotreating Catalysts and Activity for Tetralin Hydrogenation" published in *Catalysis Today* vol. 29 (1996) at pages 229-233.

It is an advantage of the present invention that the contact of organic nitrogen compounds of the entire naphtha feed are restricted from contact with the catalysts used in the hydrotreating. It is particular advantage that the catalytic distillation reaction allows the separation of the feed, into a lighter portion for hydrotreating and concentration of the organic nitrogen compounds into a heavier portion of the feed

3

comprising less than the entire feed, thereby allowing a smaller volume of the feed which constitutes the gasoline product to have to contact the organic nitrogen compound adsorbent. It is a feature of the present invention that both the hydrodesulfurization catalyst and the thioetherification catalyst are protected from contact with the organic nitrogen compounds. These and other advantages and features will become obvious from the following descriptions.

SUMMARY OF THE INVENTION

Briefly the invention comprises the treatment of a full boiling range naphtha (boiling in the range of C_5 to about 420°F) under catalytic distillation conditions to remove organic sulfur compounds in which mercaptans are removed by thioetherification while at the naphtha is concurrently split into a light fraction boiling in the range of C_5 to 160°F which is taken as overheads and a heavy fraction boiling in the range of 160-420°F which is taken as bottoms. The thioetherification catalyst is located in the upper portion of the column where the light naphtha fraction migrates and where mercaptans and olefins, preferably diolefins, are reacted to form heavier sulfide products which drop into the bottoms comprising the heavy naphtha fraction. The bottoms are treated to remove organic nitrogen compounds, preferably by passing it through an adsorber unit wherein most of the organic nitrogen compounds are adsorbed from the stream. The effluent from the organic nitrogen removal unit is then fed along with hydrogen to a second distillation column reactor containing a hydrodesulfurization catalyst wherein most of the organic sulfur compounds are converted to hydrogen sulfide. If desired the bottoms effluent from the second distillation column reactor and/or amid range naphtha sidedraw from the first distillation column reactor, after hydrogen sulfide removal, may be fed to a polishing reactor to obtain the desired level of desulfurization.

The removal of the organic nitrogen compounds from the feed to the hydrodesulfurization reactor benefits the process in three ways:

1. Higher catalyst activity on the order of 20-50% is possible;

2. The selectivity of the system will improve permitting lower olefin conversion for any given level of desulfurization; and

3. Catalyst life will be improved.

As used herein the term "distillation column reactor" means a distillation column which also contains catalyst such that reaction and distillation are going on concurrently in the column. In a preferred embodiment the catalyst is prepared as a distillation structure and serves as both the catalyst and distillation structure. The term "reactive distillation" is used to describe the concurrent reaction and fractionation in a column. For the purposes of the present invention, the term "catalytic distillation" includes reactive distillation and any other process of concurrent reaction and fractional distillation in a column regardless of the designation applied thereto.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE is a flow diagram in schematic form of the preferred embodiment of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The benefit of the of employing a catalytic distillation mode in conjunction with the nitrogen adsorption, is that the stream is split and the organic nitrogen compounds which are characteristic of the naphtha tend to largely fall in the boiling range of the heavy naphtha. The light naphtha fraction which is substantially free of the organic nitrogen compounds is not sent through the adsorption, thus reducing the load on the adsorption facility which reduces cost of installation and operation. The nitrogen containing compounds found in full boiling range cracked naphthas may include nitriles, carbazoles, benzocarbazoles, indoles, pyridines, quinolines, acridines and tetrahydroquinolines and are characterized as naturally occurring polar compounds.

Cracked naphtha is the preferred feed to the process of the instant invention because it has the desirable light olefins and the undesirable nitrogen and sulfur compounds. A typical fluid cracked naphtha boils in the range of C_5 to about 420°F and contains typically mercaptans and the lighter thiophenic compounds. The lower boiling (C_5 -about 160°F) portion of the naphtha which contains most of the valuable olefins is therefore not subjected to hydrodesulfurization catalyst but to a less severe treatment wherein the mercaptans contained therein are reacted with diolefins contained therein to form sulfides (thioetherification) which are higher boiling and can be removed with the heavier naphtha. Typically the reaction is carried out over a

nickel or palladium catalyst in the presence of hydrogen in a naphtha splitter where a light fraction is taken overhead and a heavy fraction is taken as bottoms. Advantageously the sulfides are removed with the bottoms which are eventually subjected to hydrodesulfurization.

THIOETHERIFICATION

5   A suitable catalyst for the reaction of the diolefins with the mercaptans is 0.4 wt.% Pd on 7 to 14 mesh Al_2O_3 (alumina) spheres, supplied by Süd-Chemie, designated as G-68C. Typical physical and chemical properties of the catalyst as provided by the manufacturer are as follows:

TABLE I

Designation	G-68C
Form	Sphere
Nominal size	7x14 mesh
Pd. wt.%	0.4 (0.37-0.43)
Support	High purity alumina

15   Another catalyst useful for the mercaptan-diolefin reaction is 58 wt.% Ni on 8 to 14 mesh alumina spheres, supplied by Calcicat, designated as E-475-SR. Typical physical and chemical properties of the catalyst as provided by the manufacturer are as follows:

TABLE II

Designation	E-475-SR
Form	Spheres
Nominal size	8x14 Mesh
Ni wt.%	54
Support	Alumina

25   The hydrogen rate to the reactor must be sufficient to maintain the reaction, but kept below that which would cause flooding of the column which is understood to be the "effectuating amount of hydrogen " as that term is used herein. The mole ratio of hydrogen to diolefins and acetylenes in the feed is at least 1.0 to 1.0 and preferably 2.0 to 1.0.

30 HYDRODESULFURIZATION

The reaction of organic sulfur compounds in a refinery stream with hydrogen over a catalyst to form H_2S is typically called hydrodesulfurization. Hydrotreating is a broader term which includes saturation of olefins and aromatics and the reaction of organic nitrogen compounds to form ammonia. However, hydrodesulfurization is included and is sometimes simply referred to as hydrotreating.

5   Catalyst which are useful for the hydrodesulfurization reaction include Group VIII metals such as cobalt, nickel, palladium, alone or in combination with other metals such as molybdenum or tungsten on a suitable support which may be alumina, silica-alumina, titania-zirconia or the like. Normally the metals are provided as the oxides of the metals supported on extrudates or spheres and as such are not

10   generally useful as distillation structures.

The catalysts contain components from Group V, VIB, VIII metals of the Periodic Table or mixtures thereof. The use of the distillation system reduces the deactivation and provides for longer runs than the fixed bed hydrogenation units of the prior art. The Group VIII metal provides increased overall average activity.

15   Catalysts containing a Group VIB metal such as molybdenum and a Group VIII such as cobalt or nickel are preferred. Catalysts suitable for the hydrodesulfurization reaction include cobalt-molybdenum, nickel-molybdenum and nickel-tungsten. The metals are generally present as oxides supported on a neutral base such as alumina, silica-alumina or the like. The metals are reduced to the sulfide either in use or prior

20   to use by exposure to sulfur compound containing streams. The catalyst may also catalyze the hydrogenation of the olefins and polyolefins contained within the light cracked naphtha and to a lesser degree the isomerization of some of the mono-olefins. The hydrogenation, especially of the mono-olefins in the lighter fraction may not be desirable.

25   The properties of a typical hydrodesulfurization catalyst are shown in Table I below.

TABLE III

Manufacture	Criterion Catalyst Co.
Designation	C-448
Form	Tri-lobe Extrudate
Nominal size	1.2 mm diameter

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Metal, Wt.%
        Cobalt  2-5%
        Molybdenum  5-20%
Support                    Alumina
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The catalysts typically are in the form of extrudates having a diameter of 1/8, 1/16 or 1/32 inches and an L/D of 1.5 to 10. The catalyst also may be in the form of spheres having the same diameters. They may be directly loaded into standard single pass fixed bed reactors which include supports and reactant distribution structures. However, in their regular form they form too compact a mass and must then be prepared in the form of a catalytic distillation structure. The catalytic distillation structure must be able to function as catalyst and as mass transfer medium. The catalyst must be suitably supported and spaced within the column to act as a catalytic distillation structure. In a preferred embodiment the catalyst is contained in a woven wire mesh structure as disclosed in U.S. Pat. No. 5,266,546, which is hereby incorporated by reference. More preferably the catalyst is contained in a plurality of wire mesh tubes closed at either end and laid across a sheet of wire mesh fabric such as demister wire. The sheet and tubes are then rolled into a bale for loading into the distillation column reactor. This embodiment is described in U.S. patent 5,431,890 which is hereby incorporated by reference. Other catalytic distillation structures useful for this purpose are disclosed in U.S. patents 4,731,229, 5,073,236, 5,431,890 and 5,730,843 which are also incorporated by reference.

The conditions suitable for the desulfurization of naphtha in a distillation column reactor are very different from those in a standard trickle bed reactor, especially with regard to total pressure and hydrogen partial pressure. Typical conditions in a reaction distillation zone of a naphtha hydrodesulfurization distillation column reactor are:

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Temperature            450-700 °F
Total Pressure         75-300 psig
H2 partial pressure    6-75 psia
LHSV of naphtha        about 1-5
H2 rate                10-1000 SCFB
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The operation of the distillation column reactor results in both a liquid and vapor phase within the distillation reaction zone. A considerable portion of the vapor is hydrogen while a portion is vaporous hydrocarbon from the petroleum fraction. Actual separation may only be a secondary consideration.

Without limiting the scope of the invention it is proposed that the mechanism that produces the effectiveness of the present process is the condensation of a portion of the vapors in the reaction system, which occludes sufficient hydrogen in the condensed liquid to obtain the requisite intimate contact between the hydrogen and the sulfur compounds in the presence of the catalyst to result in their hydrogenation. In particular, sulfur species concentrate in the liquid while the olefins and H_2S concentrate in the vapor allowing for high conversion of the sulfur compounds with low conversion of the olefin species.

The result of the operation of the process in the distillation column reactor is that lower hydrogen partial pressures (and thus lower total pressures) may be used.

As in any distillation there is a temperature gradient within the distillation column reactor. The temperature at the lower end of the column contains higher boiling material and thus is at a higher temperature than the upper end of the column. The lower boiling fraction, which contains more easily removable sulfur compounds, is subjected to lower temperatures at the top of the column which provides for greater selectivity, that is, less hydrocracking or saturation of desirable olefinic compounds. The higher boiling portion is subjected to higher temperatures in the lower end of the distillation column reactor to crack open the sulfur containing ring compounds and hydrogenate the sulfur.

It is believed that in the present distillation column reaction is a benefit first, because the reaction is occurring concurrently with distillation, the initial reaction products and other stream components are removed from the reaction zone as quickly as possible reducing the likelihood of side reactions. Second, because all the components are boiling the temperature of reaction is controlled by the boiling point of the mixture at the system pressure. The heat of reaction simply creates more boil up, but no increase in temperature at a given pressure. As a result, a great deal of control over the rate of reaction and distribution of products can be achieved by regulating the system pressure. A further benefit that this reaction may gain from

9

distillation column reactions is the washing effect that the internal reflux provides to the catalyst thereby reducing polymer build up and coking. Finally, the upward flowing hydrogen acts as a stripping agent to help remove the H_2S which is produced in the distillation reaction zone.

The adsorption unit may be a dual fixed bed with one bed adsorbing while the other is desorbing. The adsorption unit may also be a fluidized bed with continuous withdrawal and regeneration of the adsorbent. The adsorbents are characterized as solid particulate materials capable of selectively adsorbing organic nitrogen compounds. Examples of available adsorbents include active alumina, acid white clay, Fuller's earth, active carbon, zeolite, hydrated alumina, silica gel and ion exchange resins. The adsorbent may be regenerated with a hot gas such as hydrogen or nitrogen.

Referring now to the FIGURE there is shown a flow diagram in schematic form of one embodiment of the invention. The naphtha is fed via flow line 101 to a first distillation column reactor 10 containing two beds 12 1nd 14 of thioetherification catalyst in the upper end or rectification section below the beds. Hydrogen is fed via flow line 101A as necessary to keep the catalyst in the hydride state. The mercaptans and diolefins in the naphtha react in the catalyst beds to form sulfides. At the same time the naphtha is split into a lower boiling fraction boiling in the range of C_5 to about 160°F which is taken as overheads via flow line 103. The overheads having most of the mercaptans removed have a reduced sulfur content. A portion of the overheads is condensed and returned to the distillation column reactor as reflux (not shown). A mid boiling range cut containing predominantly thiophene as the sulfur constituent is removed from between the beds 12 and 14 via flow line 104.

The lighter components are stripped from the naphtha in the stripping section of the distillation column reactor 10 which contains standard distillation structure 16 such as sieve trays, bubble caps or structured packing. The lighter components thus stripped out are removed with the overheads. The bottoms stream containing organic nitrogen compounds, the higher boiling sulfides and thiophenic compounds are removed via flow line 102 and fed to an adsorption unit 20 where organic nitrogen compounds are removed. The effluent from the adsorption unit 20 in flow line105 is fed to a second distillation column reactor 30 containing beds 32 and 34

of hydrodesulfurization catalyst. Hydrogen is fed below the beds via flow line 105A. The organic sulfur compounds in the effluent are reacted with the hydrogen to produce hydrogen sulfide. At the same time the effluent is split into a lower boiling fraction boiling in the range of about 160-350°F which includes the gaseous hydrogen sulfide and any lighter hydrocarbons which result in the slight hydrocracking of the feed by the catalyst. The lower boiling fraction is removed as overheads via flow line 106 and the bottoms are removed via flow line 107. A portion of the overheads is condensed and returned to the distillation column reactor as reflux as needed (not shown). The bottoms and overheads are combined in flow line 108 and passed to separation vessel 40, such as a standard distillation column, where the hydrogen sulfide is removed via flow line 109. The liquid form the separation vessel 40 is removed via flow line 110 and combined with the mid boiling range cut in flow line 104 and fed to polishing reactor 50 containing a bed 52 of hydrodesulfurization catalyst where the sulfur content is reduced to the desired level, e.g., <50 wppm. Hydrogen is fed to the polishing reactor as required via flow line 111A. Finally the effluent from the polishing reactor 50 is taken via flow line 112 to a second separation vessel where the hydrogen sulfide produced in the polishing reactor is removed via flow line 113 and the desulfurized naphtha is removed via flow line 114 and combined with the overheads in flow line 103 from the thioetherification reactor 10 in flow line 115.